

[illegible]

JC05 Rec'd PCT/PTO 09 FEB 2001

U.S. Application NO. (If known, see 37 C.F.R. 1.50)		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
09/762579		PCT/EP99/05757		LP-1799	
17 <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS	PTO USE ONLY
<b>Basic National Fee (37 C.F.R. 1.492(a)(1)-(5):</b> Search Report has been prepared by the EPO or JPO \$1,000.00  International preliminary examination fee paid to USPTO (37 C.F.R. 1.482) \$720.00 No international preliminary examination fee paid to USPTO (37 C.F.R. 1.482) but international search fee paid to USPTO (37 C.F.R. 1.445(a)(2)) \$790.00  Neither international preliminary examination fee (37 C.F.R. 1.482) nor international search fee (37 C.F.R. 1.445(a)(2)) paid to USPTO \$1070.00  International preliminary examination fee paid to USPTO (37 C.F.R. 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$98.00				\$1,000.00	
ENTER APPROPRIATE FEE AMOUNT				\$1,000.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than __ 20 __ 30 months from the earliest claimed priority date (37 C.F.R. 1.492(e))				\$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	-20 =		X \$18.00	\$	
Independent Claims	-3 =		X \$78.00	\$	
Multiple Dependent Claim(s) (if applicable)			X \$270.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$1,000.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 C.F.R. 1.9, 1.27, 1.28)				\$	
SUBTOTAL =				\$1,000.00	
Processing fee of \$130.00 for furnishing the English translations later than __ 20 __ 30 months from the earliest claimed priority date (37 C.F.R. 1.492(f))				\$	
TOTAL NATIONAL FEE =				\$1,000.00	
Fee for recording the enclosed assignment (37 C.F.R. 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. 3.28, 3.31) \$40.00 per property +				\$40.00	
TOTAL FEES ENCLOSED =				\$1,040.00	
				Amount to be refunded	\$
				Charged	\$
<p>a <input checked="" type="checkbox"/> A check in the amount of <b>\$1,040.00</b> to cover the above fees is enclosed.</p> <p>b <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>06-1110</u>. A duplicate copy of this sheet is enclosed.</p> <p><b>NOTE:</b> Where an appropriate time limit under 37 C.F.R. 1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <div style="display: flex; justify-content: space-between; align-items: flex-start; margin-top: 20px;"> <div style="width: 45%;"> <p>SEND ALL CORRESPONDENCE TO:</p> <p><b>Virgil H. Marsh</b>          Fisher, Christen &amp; Sabol          Suite 1401, 1725 K Street, NW          Washington, DC 20006</p> <p>Tel.: 202/659-2000          February 9, 2001</p> </div> <div style="width: 45%; text-align: center;"> <p style="font-size: large; font-family: cursive;">Virgil H. Marsh</p> <p style="font-size: small;">SIGNATURE</p>    <p style="font-size: small;">Virgil H. Marsh</p> <p style="font-size: x-small;">NAME</p>    <p style="font-size: small;">23,083</p> <p style="font-size: x-small;">REGISTRATION NUMBER</p> </div> </div>					

09/762579 PCT/EP99/05757 LP-1799

09/762579

JC05 Rec'd PCT/PTO 09 FEB 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Docket: LP-1799

Applicant : DAUM, Ulrich, et al.  
Serial No. : Not yet assigned  
[National Stage Based Upon  
PCT/EP99/05757]  
Filed : February 9, 2001  
For : UNSATURATED OLIGOPHENOL CYANATES

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Please amend this application as follows:

**IN THE SPECIFICATION:**

On page 1, between the title and the first line of the specification, insert the following:

-- This application is a continuation (national stage) application of International (PCT) Patent Application No. PCT/EP99/05757, filed on August 9, 1999, which is a continuing application of U.S. Provisional Application Serial No. 60/096,253, filed on August 12, 1998.--

09/762579

The continuation/continuing application history of the application has been inserted on page 1 of the application.

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JC05 Rec'd FCT/FTC 09 FEB 2004

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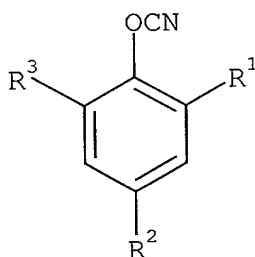
Unsaturated oligophenol cyanates

**Unsaturated oligophenol cyanates**

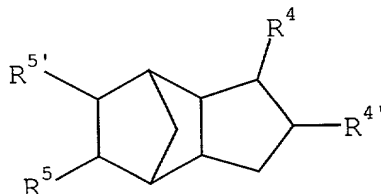
The Invention relates to oligophenol cyanates of the general formula



In this formula, A is in each case a group of the formula



and B is in each case a group of the formula



R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> on each group A independently of the others are in each case hydrogen or a bond to a group B with the proviso that each group A has either one or two bonds to B.

Both R<sup>4</sup> and R<sup>4'</sup>, and R<sup>5</sup> and R<sup>5'</sup>, on each group B independently of the others, are in each case either together a direct bond or, in any desired order, are hydrogen and a bond to a group A with the proviso that each group B has either one or two bonds to A.

The indices *m* and *n* are 0 or 1 and *x* is an integer from 0 to 10 with the proviso that at least one of the numbers *m*, *n* and *x* is other than 0 and *m* and *n* are not both at the same time 1.

The Invention also relates in particular to mixtures of such compounds with one another and/or with those compounds of the

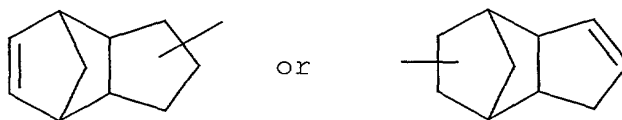
formula I in which  $m$  and  $n$  deviate from the above definitions by both being 1.

Saturated oligophenol cyanates of general formula I in which  $m$  and  $n$  deviate from the compounds of the present invention by both being 1 are known, for example, from EP-A-0 147 548 and are marketed by the Dow Chemical Co. under the designation XU71787. These compounds do not have any olefinic double bonds and are therefore able to polymerize only by cyclotrimerization of the cyanate groups or by reaction with functional groups of other compounds. The cyclotrimerization requires the presence of catalysts and/or high temperatures. In contrast it is often desirable to achieve partial curing or crosslinking by means, for example, of irradiation at room temperature. In addition, these known compounds have a relatively high viscosity, which is unfavourable for some applications.

The object of the present invention was therefore to provide oligophenol cyanates which have a low viscosity and which without further additives can be (partially) polymerized or crosslinked at room temperature by means, for example of radiation-induced free-radical reactions.

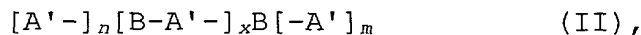
In accordance with the invention this object is achieved by the unsaturated oligophenol cyanates of the formula I in accordance with Claim 1. The molecule of these compounds has at least one olefinic double bond ( $R^4-R^{4'}$  and/or  $R^5-R^{5'}$  according to formula I) which permits free-radical addition polymerization.

The olefinic double bonds are present in groups of the formula

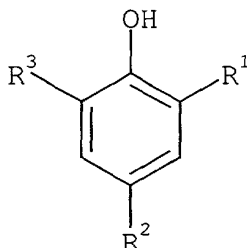


The degree of polymerization,  $x$ , lies preferably between 0 and 5 and, with particular preference, between 0 and 3.

The unsaturated oligophenol cyanates of the invention can be prepared by reacting an oligophenol of the general formula



in which A' is a group of the formula



and B, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>4'</sup>, R<sup>5</sup>, R<sup>5'</sup>, m, n and x are as defined in Claim 1, is reacted with cyanogen chloride in the presence of a tertiary amine. Oligophenols of formula II are obtainable from Borden Chemical Inc. under the designations ESD-X1 to -X5, ESD-472C and ESD-473C. The compounds concerned here are condensation products of dicyclopentadiene (dimeric cyclopentadiene) and phenol, which are present as a mixture of isomeric and/or homologous compounds and also contain fractions of saturated compounds where m = n = 1.

The preparation of the oligophenol cyanates of the invention is preferably carried out at a temperature of less than 10 °C in a polar solvent such as butyl acetate and/or acetone or methyl ethyl ketone, for example, or in mixtures of these solvents. Particularly preferred reaction temperatures are below 0 °C - for example, -10 °C. It is advantageous to employ 1.0-1.1 mol of tertiary amine and 1.0-1.2 mol of cyanogen chloride per OH equivalent of the oligophenol II. A particularly preferred tertiary amine is triethylamine.

The unsaturated oligophenol cyanates of the invention have a low viscosity at processing temperature and produce polytriazine resins having a particularly low dielectric constant. They are particularly suitable, for example, as matrix material for the production of fibre-reinforced composites, especially for



components in aerospace technology, or as base materials for the production of printed circuit boards. Owing to their low viscosity and capacity for polymerization by means of high-energy radiation (UV, X-rays,  $\gamma$ -rays or electron beams), they are also suitable for (photo)lithographic varnishes, solder resists for circuit boards, or other radiation-curable lacquers and coatings.

The following example illustrates the preparation of the oligophenol cyanates of the invention without constituting any restriction.

### Example

Oligophenol ESD-X3 (Borden Chemical Inc.) was dissolved in n-butyl acetate/acetone (v/v = 80:20) to give a 15% strength solution. The solution was cooled to  $-10^{\circ}\text{C}$  and, at this temperature, 105% of the calculated amount of triethylamine and then, over the course of 30 minutes, 110% of the calculated amount of cyanogen chloride were added. After a further 30 minutes of reaction, the mixture was subjected to extraction with water, twice at  $30^{\circ}\text{C}$ , in order to remove the ammonium salts formed, and was then passed twice through a falling-film evaporator in order to remove the solvent and the by-product, *N,N*-diethylcyanamide.

Yield: about 100%

### Properties:

viscosity: 165 mPa·s (at  $125^{\circ}\text{C}$ )

degree of reaction: (phenol  $\rightarrow$  cyanate) >98%

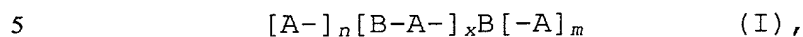
gel time: 25 min (at  $200^{\circ}\text{C}$ )

carbamates: <1%

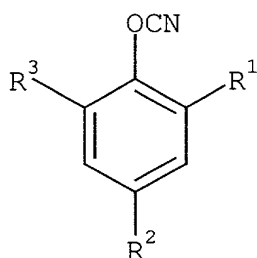
*N,N*-diethylcyanamide: <2000 ppm

# Claims

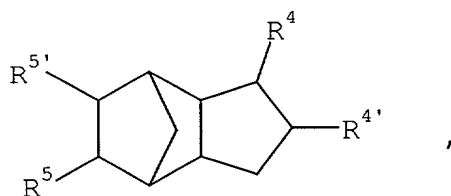
1. Unsaturated oligophenol cyanates of the formula



in which A is in each case a group of the formula



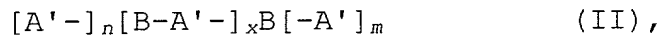
and B is in each case a group of the formula



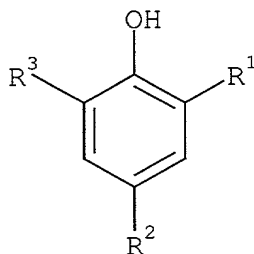
- wherein  $R^1$ ,  $R^2$  and  $R^3$  are in each case hydrogen or a bond to a group B with the proviso that each group A has either one or two bonds to B;  
 both  $R^4$  and  $R^{4'}$ , and  $R^5$  and  $R^{5'}$  are in each case either together a direct bond or are hydrogen and a bond to a group A with the proviso that each group B has either one or two bonds to A;  
 the indices  $m$  and  $n$  are 0 or 1 and  $x$  is an integer from 0 to 10 with the proviso that at least one of the numbers  $m$ ,  $n$  and  $x$  is other than 0 and  $m$  and  $n$  are not both at the same time 1, and mixtures thereof with one another and/or with those compounds of the formula I in which  $n$  and  $m$  deviate from the above definitions by both being 1.

2. Oligophenol cyanates according to Claim 1, characterized in that  $x$  is from 0 to 5.

3. Process for preparing unsaturated oligophenol cyanates according to Claim 1, characterized in that an oligophenol of the general formula



in which  $A'$  is a group of the formula



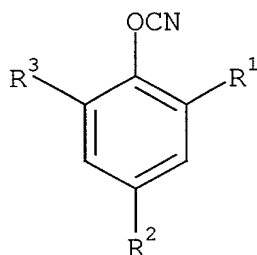
and  $B$ ,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^4'$ ,  $R^5$ ,  $R^5'$ ,  $m$ ,  $n$  and  $x$  are as defined in Claim 1, is reacted with cyanogen chloride in the presence of a tertiary amine.

4. Use of the unsaturated oligophenol cyanates according to Claim 1 as matrix material for fibre-reinforced composites.

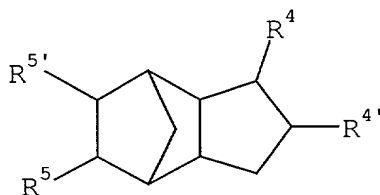
5. Use of the unsaturated oligophenol cyanates according to Claim 1 as radiation-curable varnishes, resists, lacquers and coatings.

# Abstract

The invention relates to unsaturated oligophenol cyanates of the general formula (I)  $[A-]_n[B-A-]_xB[-A]_m$  in which A is a group of formula



and B is a group of formula



where  $R^1$ ,  $R^2$  and  $R^3$  are each hydrogen or a bond with a group B, there being either one or two bonds with B; and both  $R^4$  and  $R^{4'}$  as well as  $R^5$  and  $R^{5'}$  separately or jointly represent a direct bond or hydrogen and a bond with a group A, there being either one or two bonds with A. The indices  $m$  and  $n$  are 0 or 1 but not both 1 at the same time and  $x$  is a whole number between 0 and 10, where at least one of the numbers  $m$ ,  $n$  and  $x$  is not 0.

The above unsaturated oligophenol cyanates can be prepared by reacting the corresponding oligophenols with cyanogen chloride. They have a low viscosity and owing to their double bonds are able to undergo free-radical polymerization. They are especially suitable for use as matrix materials for fibre-reinforced composites and for radiation-curable varnishes and coatings.

Type a plus sign (+) inside this box → ☐

<div style="display: flex; justify-content: space-between;"><div>0010/PTO Rev 6/95</div><div>U.S. Department of Commerce Patent and Trademark Office</div></div> <div style="text-align: center; margin-top: 20px;"><b>DECLARATION</b></div> <div style="display: flex; justify-content: space-around; margin-top: 20px;"><div><input checked="" type="checkbox"/> Declaration Submitted with Initial Filing</div><div>OR <input type="checkbox"/> Declaration Submitted After Initial Filing</div></div>	<table border="1" style="width: 100%; border-collapse: collapse;"><tr><td style="width: 60%;">Attorney Docket Number</td><td>LP-1799</td></tr><tr><td>First Named Inventor</td><td>DAUM</td></tr><tr><td colspan="2" style="text-align: center;"><b>COMPLETE IF KNOWN</b></td></tr><tr><td>Application Number</td><td></td></tr><tr><td>Filing Date</td><td></td></tr><tr><td>Group Art Unit</td><td></td></tr><tr><td>Examiner Name</td><td></td></tr></table>	Attorney Docket Number	LP-1799	First Named Inventor	DAUM	<b>COMPLETE IF KNOWN</b>		Application Number		Filing Date		Group Art Unit		Examiner Name																							
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<p>As a below named inventor, I hereby declare that:</p> <p>My residence, post office address, and citizenship are as stated below next to my name</p> <p>I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.</p> <div style="border: 1px solid black; padding: 5px; margin: 10px 0; text-align: center;"><b>UNSATURATED OLIGOPHENOL CYANATES</b></div> <p style="text-align: center; font-size: small;">(Title of the Invention)</p> <p>the specification of which</p> <div style="display: flex; align-items: center;"><div style="margin-right: 10px;"><input checked="" type="checkbox"/> is attached hereto</div><div>OR <input type="checkbox"/> was filed on (MM/DD/YYYY) <span style="border: 1px solid black; display: inline-block; width: 150px; height: 1.2em; vertical-align: middle;"></span> as United States Application Number or PCT International Application Number <span style="border: 1px solid black; display: inline-block; width: 150px; height: 1.2em; vertical-align: middle;"></span> and was amended on (MM/DD/YYYY) <span style="border: 1px solid black; display: inline-block; width: 150px; height: 1.2em; vertical-align: middle;"></span> (if applicable)</div></div> <p>I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.</p> <p>I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § .56.</p> <p>I hereby claim foreign priority benefits under Title 35, United States Code §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed</p> <table border="1" style="width: 100%; border-collapse: collapse; font-size: small;"><thead><tr><th>Prior Foreign Application Number(s)</th><th>Country</th><th>Foreign Filing Date (MM/DD/YYYY)</th><th>Priority Not Claimed</th><th colspan="2">Copy Attached?</th></tr><tr><th></th><th></th><th></th><th></th><th>YES</th><th>NO</th></tr></thead><tbody><tr><td>PCT/EP99/09477</td><td>International</td><td>08/09/1999</td><td style="text-align: center;"><input type="checkbox"/></td><td style="text-align: center;"><input checked="" type="checkbox"/></td><td style="text-align: center;"><input type="checkbox"/></td></tr><tr><td>98202692.4</td><td>Europe</td><td>08/11/1998</td><td style="text-align: center;"><input type="checkbox"/></td><td style="text-align: center;"><input checked="" type="checkbox"/></td><td style="text-align: center;"><input type="checkbox"/></td></tr><tr><td>60/096,523</td><td>U.S. Provisional</td><td>08/12/1998</td><td style="text-align: center;"><input checked="" type="checkbox"/></td><td style="text-align: center;"><input type="checkbox"/></td><td style="text-align: center;"><input checked="" type="checkbox"/></td></tr><tr><td></td><td></td><td></td><td style="text-align: center;"><input type="checkbox"/></td><td style="text-align: center;"><input type="checkbox"/></td><td style="text-align: center;"><input type="checkbox"/></td></tr></tbody></table>		Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Copy Attached?						YES	NO	PCT/EP99/09477	International	08/09/1999	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	98202692.4	Europe	08/11/1998	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	60/096,523	U.S. Provisional	08/12/1998	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>				<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
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<p>I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.</p>																																					
<b>Application Number(s)</b>	<b>Filing Date (MM/DD/YYYY)</b>	<div style="display: flex; align-items: center;"><div style="margin-right: 10px;"><input type="checkbox"/></div><div>Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.</div></div>																																			

## DECLARATION

Page 2

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations 1.56 which became available between the filing date of the prior application and the national or PCT filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
60/096,253	PCT/EP99/05757	08/09/1999 08/12/1998	

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Firm Name **Fisher, Christen & Sabol**Payor Number  
(if applicable)

Name	Registration Number	Name	Registration Number
Virgil H. Marsh	23,083		
Kara M. Armstrong	38,234		

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

☒ Please direct all correspondence to

Name
Virgil H. Marsh

Address **Fisher, Christen & Sabol**

Address **Suite 1401, 1725 K Street, N.W.**

City	State	Zip
Washington	D.C.	20006

Country	Telephone	Fax
USA	(202)659-2000	(202)659-2015

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**Name of Sole or First Inventor:**

☐ A petition has been filed for this unsigned inventor

Given Name	Middle Initial	Family Name	Suffix
Ulrich		DAUM	

Inventor's Signature *Ulrich* *Daum*

Residence: City	Country	Citizenship
Hofstetten	Switzerland	German

Post Office Address: **Chöpfliweg 17**

City	Postal Code	Country	Applicant Authority
Hofstetten	CH-4114	Switzerland	

☒ Additional inventors are being named on supplemental sheet(s) attached hereto.

